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RESEARCH IN TRACE EMISSION SPECTROSCOPY

FINAL REPORT

FEBRUARY 28, 1962

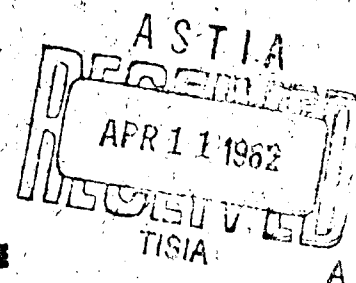
PROJECT 4608

TASK 46084

CONTRACT NO. AF19(604)-8013

SUBMITTED TO

ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS



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Task 46086

Contract No. AF19(604)-8013

Prepared for

Electronics Research Directorate
Air Force Cambridge Research Laboratories
Office of Aerospace Research
United States Air Force
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ABSTRACT

This final report summarizes the research accomplishments under Contract No. AF19(604)-8013 during the period from 2/1/61 to 2/1/62. The research information obtained from this study has (a) resulted in a reliable analytical method for the determination of trace impurities in gallium arsenide, (b) extended the understanding of the influence of matrix volatility so that techniques can be varied to suit the matrix volatilization behavior, (c) clarified the problem of the preparation of representative standards and (d) by the combination of emission spectroscopy, mass spectroscopy and wet chemical analyses pointed the way to maximum effectiveness in the solution of ultratrace analytical problems.

1. INTRODUCTION

The emphasis on semiconductor and high purity materials technology in the electronics industry has stimulated the development of trace emission spectrographic methods of analysis that are convenient, sensitive and reliable. These methods are essential to the development of ultrapurification techniques and provide better insight into the role of impurities in the electrical properties of these materials.

Previous work on the spectrographic determination of trace impurities in semiconductor grade silicon carbide^{1, 2} and high purity electronic nickel³ showed that the emission spectrograph could determine impurities in these materials in the parts per billion concentration range by taking advantage of differences in volatilization rates between impurities and matrix. These matrix materials were of low volatility. The present investigations were conducted on the volatile semiconductor, gallium arsenide, to determine the effects of matrix volatility on spectrographic sensitivity and to develop a reliable analytical method for the determination of trace impurities in this material.

Gallium arsenide is a high temperature semiconductor possessing the unique properties of high n-type mobility, short lifetime (μsec range), direct recombination with no relaxation time, a low dielectric constant (~ 11) and a high energy gap (~ 1.45 eV). These electrical properties are indicative of potentially improved transistor action and high speed switching capabilities when the state of the materials fabrication art is sufficiently advanced. It has been shown in this laboratory that the electrical properties of gallium arsenide are not indicative of chemical purity and cannot be used as a reliable basis for an empirical approach to device fabrication. Accordingly, the development of reliable sensitive trace

methods of analyses for impurities in this material are essential to the evolution of these arts.

2. RESEARCH

A systematic investigation of the factors necessary for the development of a trace spectrographic method for the determination of impurities in gallium arsenide was made. These factors are -

1. The volatilization behavior of gallium arsenide.
2. The volatilization behavior of impurities from the gallium arsenide.
3. The effect of matrix volatility on spectrographic sensitivity.
4. The preparation of representative standards.
5. The preparation of spectrographic working curves of impurities in gallium arsenide.
6. The spectrographic method for the determination of trace impurities in gallium arsenide.

2.1 VOLATILIZATION BEHAVIOR OF GALLIUM ARSENIDE

Of prime importance in the development of a trace analytical method for the determination of impurities by emission spectroscopy is a knowledge of the volatilization behavior of the matrix and the impurity elements of interest. Use is made of the differences in volatilization rates to optimize spectrographic sensitivity. Gallium arsenide starts to dissociate at 500°C, producing large volumes of arsenic vapor, thereby rendering the control of dissociation and volatilization more difficult.

2.1.1 Inert Atmosphere Study

The use of enclosed inert gas atmospheres to control volatilization of GaAs results in varied dissociation-volatilization behavior according to the power input to the arc. The use of low power input (100 watts, dc) results in marked dissociation of the gallium arsenide with accompanying attenuation of the light transmitted to the spectrograph by the condensed arsenic vapor. The time for complete volatilization of a 50 mg sample is 6-10 minutes. The attenuation of the light and the lengthy volatilization time work against high spectrographic sensitivity. If the exit port of the chamber is enlarged to remove the arsenic vapor, erratic heating conditions are produced due to the exothermic reaction of the electrode cup with air which leaks back into the chamber and also to the unstable voltage drops across the arc.

On the other hand, the use of high power input (400 watts, dc) in the arc in inert atmospheres reduces the dissociation of GaAs. The sample is completely consumed in 3-6 minutes with no attenuation of the light transmitted to the spectrograph. A serious limitation to the use of this approach is the appearance of the impurity lines at unreproducible intervals while volatilization is taking place.

An explanation of these results can be made by considering the pressure-temperature-composition phase diagrams for GaAs^4 (see Fig. 1). Low power input results in small temperature rise per unit time permitting the temperature of the gallium arsenide to slowly rise to 810°C at which point the equilibrium vapor pressure of arsenic is 29 atmospheres. The result is a violent thermal decomposition. High power input causes a large temperature rise per unit time of the gallium arsenide bringing the temperature to the melting point of gallium arsenide (1230°C) at which

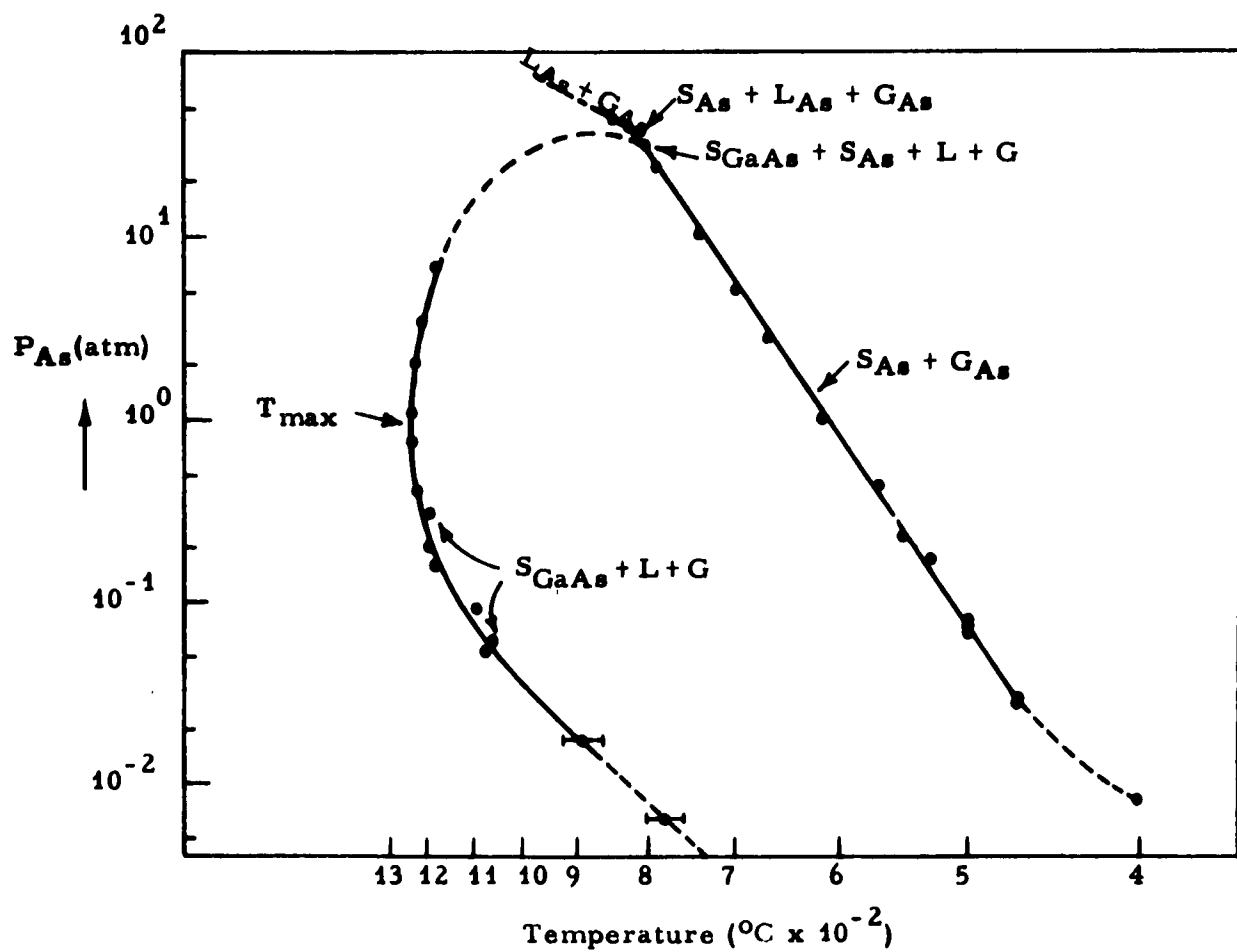


Fig. 1. Vapor pressure curve of GaAs⁽⁴⁾

point the equilibrium vapor pressure of arsenic above gallium arsenide is 0.9 atmospheres. A controlled thermal dissociation takes place.

The use of a high frequency ac spark source resulted in violent thermal dissociation of the gallium arsenide because of the intermittent low power input to the arc.

The use of inert atmospheres was discontinued because the conditions could not be rigorously controlled to provide reproducible burns.

2.1.2 Total Burn-Total Energy Study

With the dissociation of the gallium arsenide into arsenic vapor and gallium metal, the solubility of many of the impurity elements in molten gallium becomes a factor. Some of these elements volatilize with the gallium but many do not volatilize until all the gallium has been distilled. In order to observe the above impurities following closely upon those elements that volatilize with the arsenic, a total burn-total energy approach was used. This approach was to employ a micro sample (0.5 mg) in a small graphite electrode cup with a large power input (1200 watts, dc) to cause the instantaneous volatilization of the sample into the arc. The results of this method were inconclusive due to a marked increase in sensitivity for impurity elements in the graphite electrodes. This increased electrode blank coupled with the problem inherent in obtaining homogeneous micro samples of matrix material and standards precluded further work in this direction.

2.1.3 Controlled Dissociation Study

The final approach to the study of volatilization behavior of GaAs involved improved control of the dissociation in air so that mechanical entrainment of impurities in the arsenic vapor stream is reduced. The

method consists of two parts: (1) the determination of impurities that volatilize with the arsenic and (2) the determination of impurities that remain behind in the molten gallium. The conditions that minimize mechanical entrainment conflict with the conditions necessary for high sensitivity so that a compromise must be made in precision and accuracy vs sensitivity. This was the approach selected to develop the optimal analytical methods for the determination of trace impurities in gallium arsenide.

Gallium arsenide spectra taken in air have extensive molecular band structure due to the oxides of arsenic and gallium that are formed in the mantle of the arc. The oxide and cyanogen band structure in addition to a heavy continuum renders the wavelength regions of 3200-3450A and 3900-4000A useless for trace spectroscopy. The remainder of the spectrum can be used provided the exposure times are short (10-30 sec) with Eastman Kodak 103-O and 103-F plates.

The spectrographic conditions for the method are shown in Table I. Samples of gallium arsenide (0.045 g) were burned under these conditions and the burn times were varied so that the rate at which the gallium arsenide was consumed could be determined. A curve showing the loss in weight as a function of the burn time is shown in Fig. 2. The arsenic is completely volatilized in the first ten seconds at a rate of 2.84×10^{-3} g/sec while the gallium requires an additional fifty seconds at a rate of 4.56×10^{-4} g/sec. The curve in Fig. 3 is a plot of the intensities of the gallium 2607A and the arsenic 2381A lines as a function of burn time and corroborates the rate data. These arcing conditions provide good reproducibility of intensity ratios in the 0-10 second and the 20-60 second intervals. The time interval 10-20 seconds should not be used due to varying arsenic concentration in the arc.

TABLE I

CONDITIONS OF SPECTROGRAPHIC ANALYSIS

Special Equipment: Bausch & Lomb Dual Grating Spectrograph with 426 mm
f.l. cover lens. The arc box is fitted with a rotating
electrode holder which rotates the anode at 50 rpm.

Source to slit distance:	56 cm
Slit Width:	50 microns
Current:	10 amperes, dc
Analytical Gap:	4 mm
Electrode:	Anode United Carbon No. 425 Cathode United Carbon No. 1966 or Anode National Carbon SP1001 Cathode National Carbon SP1004
Photographic Plate:	Eastman Kodak 103-0
Spectral Range:	2300-3400A

ANALYTICAL LINES AND OPTIMUM EXPOSURE INTERVAL

Cd	3261.06	0-10 sec.
Si	2516.1	0-10 sec.
Te	2385.8	0-10 sec.
Zn	3345.0	0-10 sec.

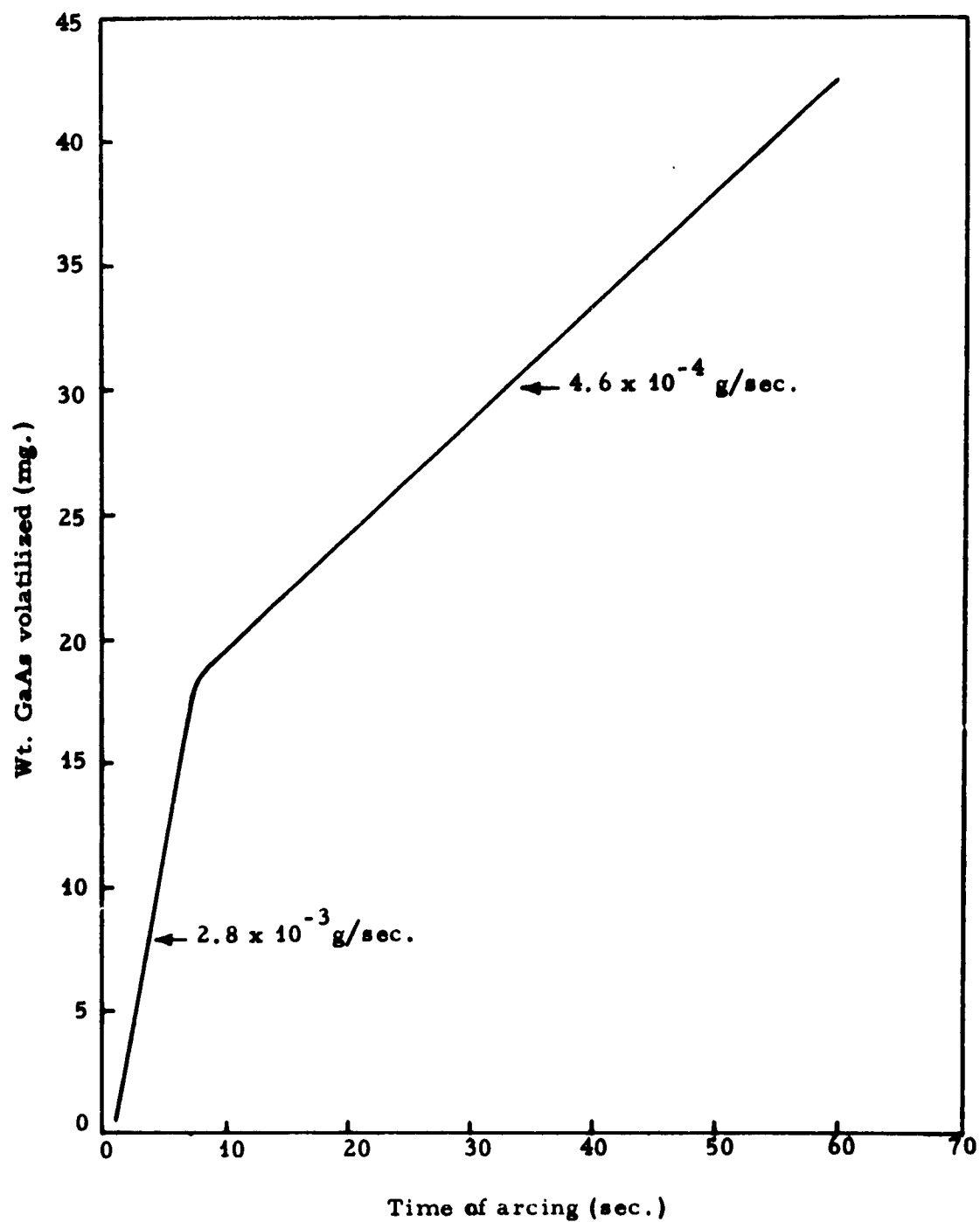


Fig. 2. Volatilization behavior of GaAs.

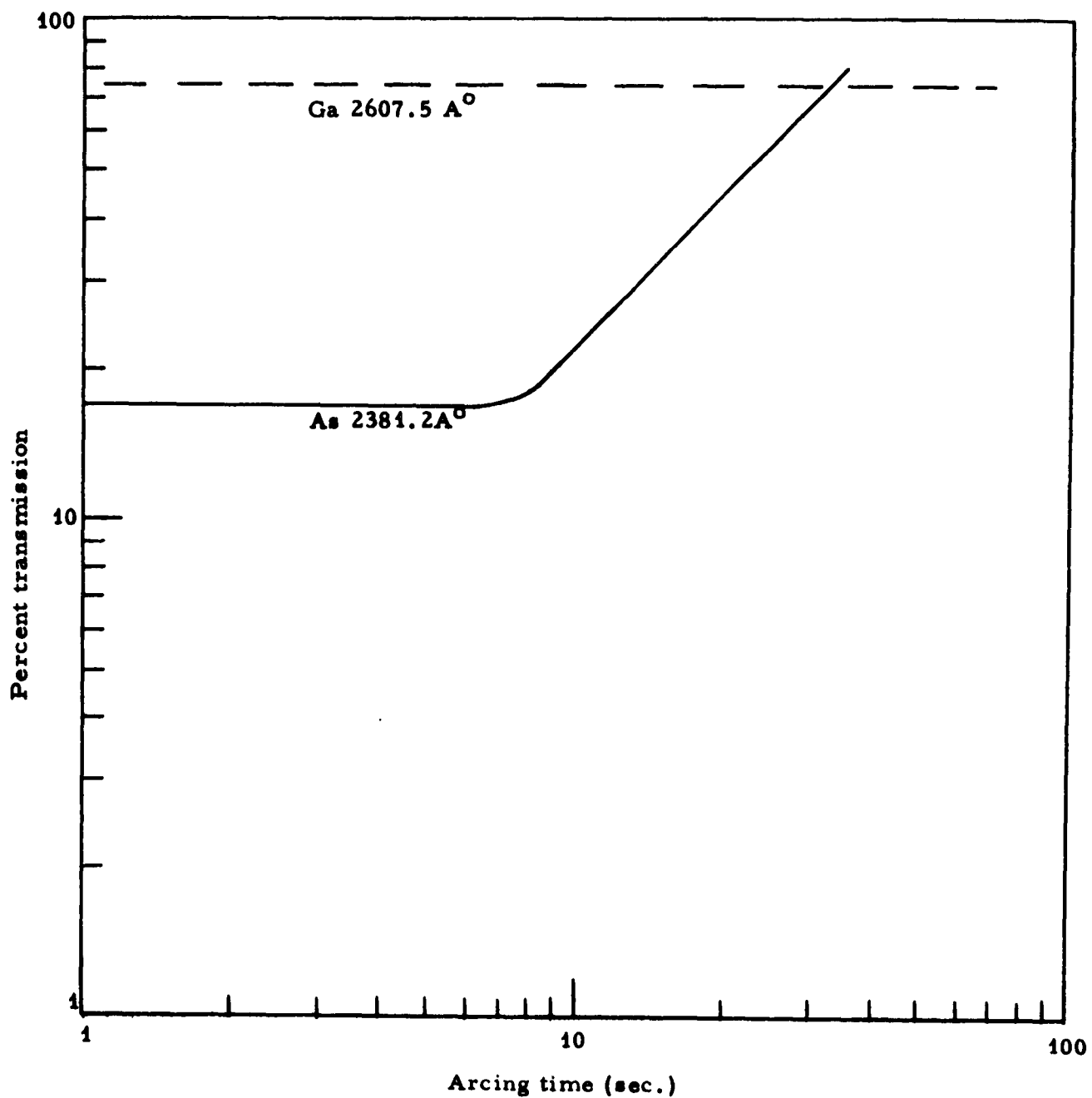


Fig. 3. Matrix line intensities -- volatilization study.

2.2 VOLATILIZATION BEHAVIOR OF IMPURITIES FROM GALLIUM ARSENIDE

The volatilization of an impurity from any matrix during the arcing is a complex process dependent upon the chemical nature and concentration of the impurity, its solubility condition in the matrix, its chemical reactivity with the matrix, carbon and other impurities at elevated temperatures and its thermodynamic properties under these conditions. Assuming that excitation conditions are constant during the arcing process, the volatilization behavior of impurities in a matrix is studied by moving the spectrographic plate in a direction parallel to the spectrograph slit during the arcing. Care must be taken to use a small Hartman opening on the slit with a slow rate of plate traverse ($\sim 1-2\text{mm/sec}$). Too fast a plate traverse can spread the impurity lines so that they are indistinguishable from background.

2.2.1 Moving Plate Study

Moving plate studies were performed on gallium arsenide which contained impurities as oxides, elemental powders and in solid solution at various concentrations. The volatilization behavior of some impurities was markedly different when in solid solution compared to the case where the same impurities were present as mixtures of finely divided oxide or elemental powder blended with pulverized GaAs. For instance, tellurium and silicon as the oxides TeO_2 and SiO_2 at 100 parts per million required up to 60 seconds for complete evolution under conditions in Table I, at a rate which increased toward the end of the burn. Tellurium and silicon in solution at 2000 and 40 parts per million respectively required up to 20 seconds for complete evolution under identical conditions. On the other hand, zinc and cadmium in solid solution at 100 parts per million required up to 10 seconds for complete volatilization which was close to the time

required for volatilization of these impurities as oxides in a physical mixture. A comparison of the working curves Figs. 4 and 5 will show that the oxide standards are not generally representative of the impurity behavior in solid solution even though the volatilization rates were seemingly identical.

The disappearance of a spectral line does not mean that the element has completely volatilized. There exists the possibility that a portion of the impurity volatilized or was mechanically entrained during the approximately 20 seconds in which dissociation takes place. The rate of entry into the arc stream initially would be proportional to the product of the mole fraction in the gallium arsenide and the rate of dissociation of the gallium arsenide. At the end of the first twenty seconds, the impurity may be in solution in the molten gallium where its volatilization rate is proportional to the product of the mole fraction and the partial vapor pressure of the impurity at the boiling point of the gallium. The difference in rate would be sufficient to reduce the intensity of the line below detection. An example of this is boron in gallium arsenide. The grinding of gallium arsenide in a boron carbide mortar introduces boron as a contaminant in the matrix. The boron appears to completely volatilize in the 0-10 second time interval. No boron lines appear again until all the gallium has been volatilized. Similar results were obtained with iron, copper and aluminium as the oxide powders. To obtain a reproducible internal standard line, it is necessary to exclude the time interval during arcing when the concentration of either of the matrix elements in the arc is changing rapidly. The periods from 10-20 seconds and after 60 seconds produce wide variation in intensity ratios. During the 10-20 second interval the arsenic content of the arc decreases rapidly due to depletion of the arsenic. The period after 60 seconds is marked by rapid decrease

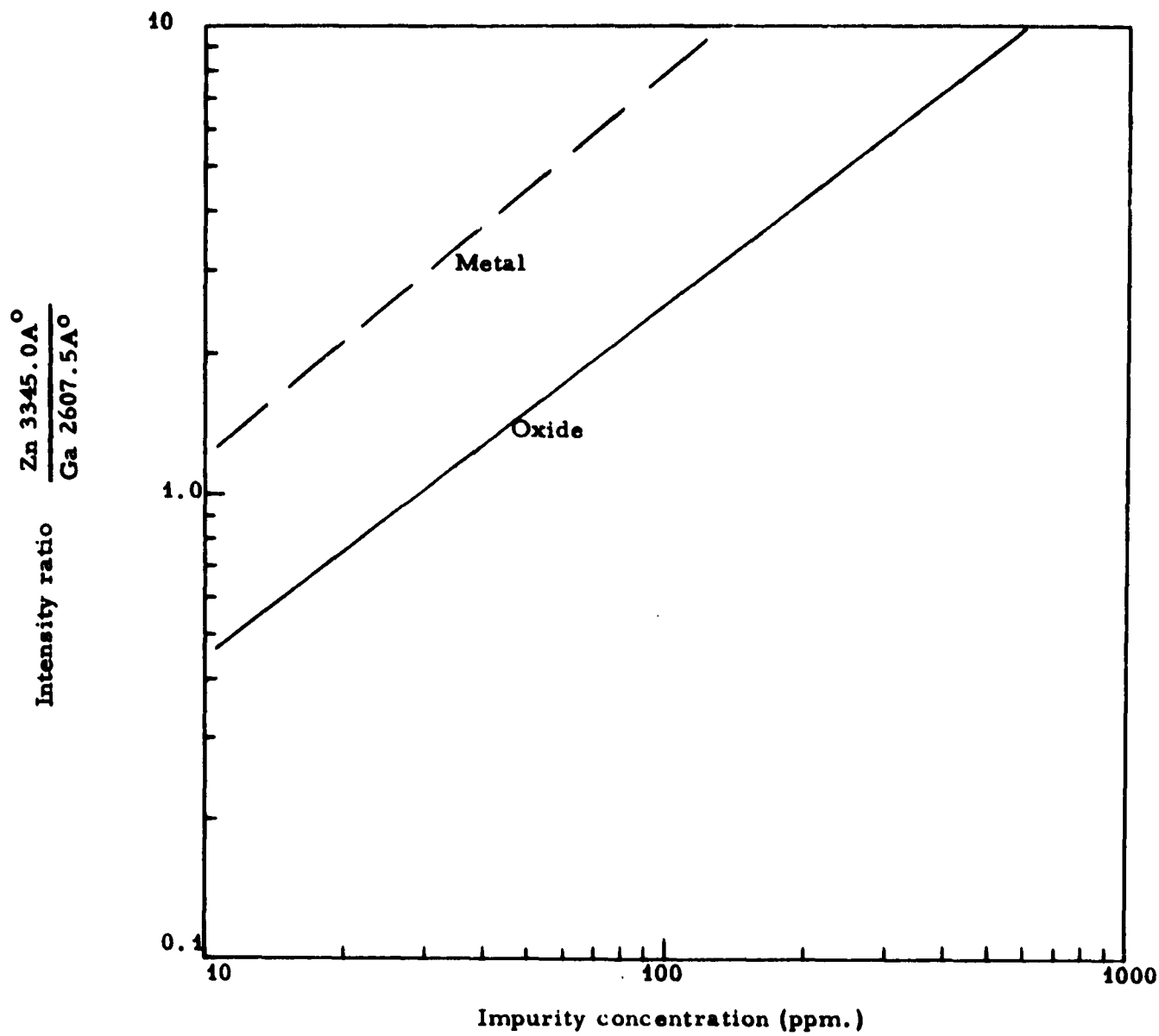


Fig. 4. Spectrographic working curves -- powder dilution stds. in GaAs

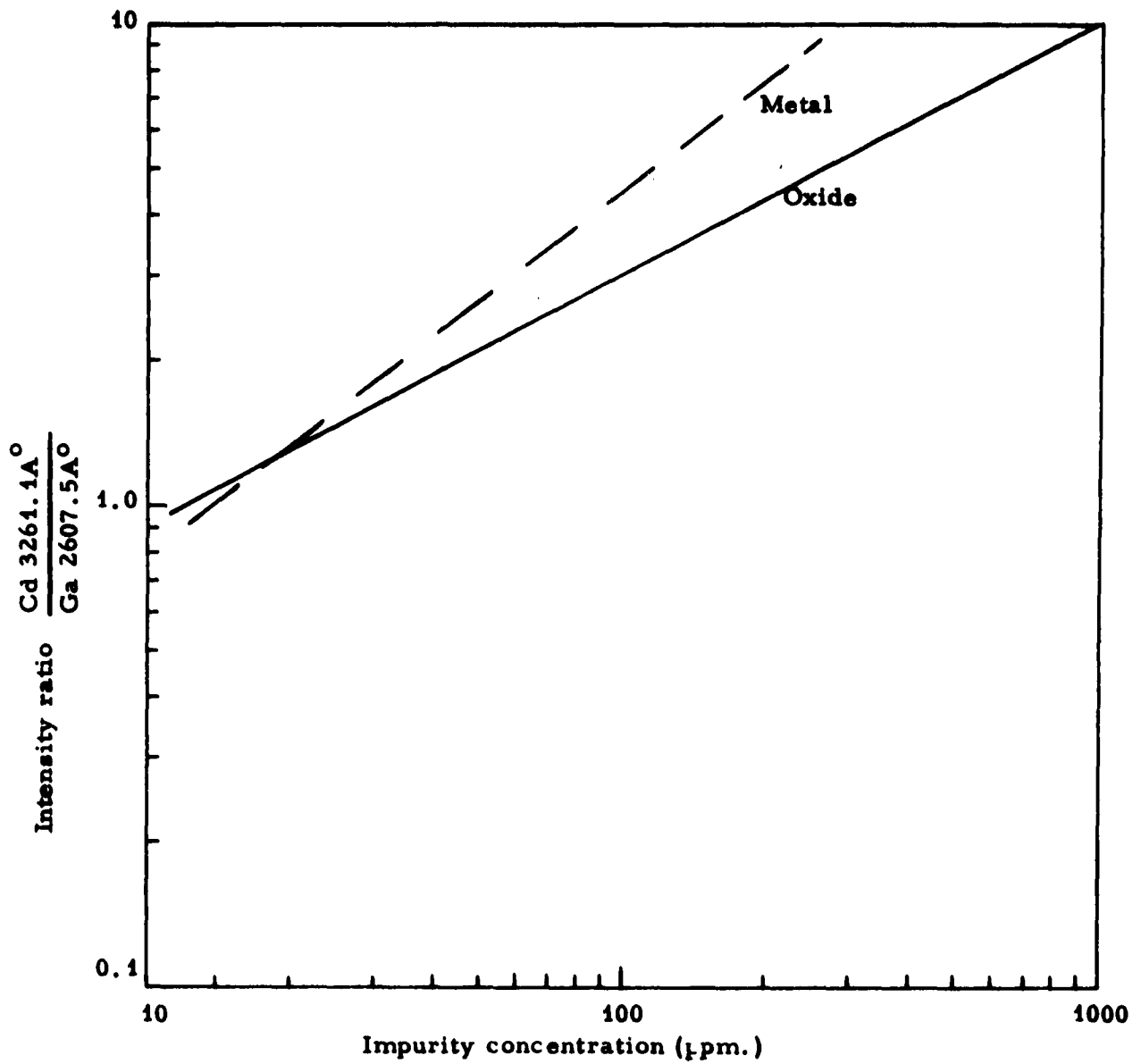


Fig. 5. Spectrographic working curves -- powder dilution stds. in GaAs

of gallium due to depletion. Accordingly the exposure time for Cd, Zn, Si and Te, which volatilizes with the arsenic, was taken from 0-10 seconds. Data for the oxide and metallic impurity standards prepared by powder dilution have been previously reported. Working curves prepared from these standards have proven not representative of the gallium arsenide system, as shown in the preceding section.

2.3 EFFECT OF MATRIX VOLATILITY ON SPECTROGRAPHIC SENSITIVITY

The work on gallium arsenide as a volatile matrix coupled with experience with the refractory or low volatility silicon carbide and nickel, representing intermediate volatility, provides a basis for generalizations concerning the effects of matrix volatility on spectrographic sensitivity.

2.3.1 Dissociative Matrices

Matrix materials that dissociate and are in a finely powdered form release many impurities into the arc stream before extensive sintering takes place. This fact has been borne out in the studies on gallium arsenide and silicon carbide. During the dissociation of gallium arsenide and before sintering and melt take place, many impurities (i. e., B and Si) enter the arc stream that would not normally enter the arc from a molten solution at the same temperature. The study on silicon carbide showed extensive selective volatilization, the factor responsible for high spectrographic sensitivity. Silicon carbide did not sinter or melt, permitting thereby the fractionation of impurity groups according to volatility. This was an ideal case wherein the power input into the arc permitted the electrode cup temperature to come to equilibrium at the dissociation temperature of silicon carbide ($\sim 2400^{\circ}\text{C}$). Therefore, the background contribution from the electrodes was kept at the minimum necessary to assure dissociation. Attempts were made in the nickel study to control

the sintering of the fine nickel powder to simulate dissociation behavior. The expected trend was observed; however, sufficient control of the arcing and sintering was not possible for the development of an analytical method using this technique. It was found that the intensity of the impurity lines is dependent upon particle size while the intensity of the matrix lines are independent of particle size. Thus, this system requires rigorous control of a sample parameter which is not at the disposal of the spectroscopist.

2.3.2 Volatile Matrices

The temperature rise in the electrode cup is in the order of 1000°C in the first second with low power input in inert atmospheres. If the boiling point of the matrix material is less than 1000°C , the temperature of the matrix will be constant at the boiling point. The sensitivity for impurities that are very volatile relative to the matrix is poor because of the time lag between volatilization and excitation. (See TR60-703.8). The sensitivity approaches 100 parts per million as the lower limit of detection. Impurities that have about the same volatility as the matrix have sensitivities that will vary according to the technique used in the choice of exposure times. If the matrix contributes many lines and poor background (band structure, etc.) it is wise to choose an aliquot of the volatilization time for the exposure time. This has produced very good results in the case of nickel but is dependent upon the number of impurities to be determined and the mean sensitivity required of the analysis. The time of volatilization of the matrix can be used as the exposure time (total burn technique) and this too can be varied by power input into the arc and by size of sample used.

The technique used is a matter of personal preference and is dependent upon the efficiency of the external optical train of the spectrograph and the photographic plate used as the detector. The limit of

detection for impurities which have the same volatility as the matrix is in the range of 10-100 parts per million. Impurities that are more refractory than the matrix require complete volatilization of the matrix before they volatilize into the arc stream. In common practice they are recorded on the same exposure as the matrix and other impurities in order to provide matrix lines as internal standards. Care must be taken to extinguish the burn when matrix volatilization is complete because the controlling influence of the matrix vaporization is complete and the temperature of the electrode cup rises sharply, thereby increasing background. The refractory impurities have limits of detection approximating 100 parts per million.

2.3.3 Refractory Matrices

The recent interest in the spectrographic analysis of refractory materials is a result of the military need for high temperature materials. Since high temperature is needed for volatilization and can only be achieved in the spectrographic arc by high power input in reactive gas atmospheres (O_2 , N_2) that react with the electrodes exothermally to produce heavy background, most refractories are either finely powdered or are chemically changed to form more volatile compounds. The refractory metals contribute very many matrix lines to the spectrum because of the large number of electrons in the outer ring and the many possible transitions. The volatile compounds of the refractory materials are changed in the arc to refractory carbides by admixture with carbon powder. This decreases matrix spectra permitting the determination of impurity concentration. Many of the refractory materials are extremely hard and cannot be powdered without the introduction of large amounts of impurities. The most difficult spectrographic problem lies in the determination of trace refractories in a refractory matrix because of the similarities in chemistry and chemical reactivity to form refractory carbides.

2.4 PREPARATION OF SPECTROGRAPHIC STANDARDS OF IMPURITIES IN GALLIUM ARSENIDE

The preparation of representative standards is the basis for the reliability of any method of analysis. In emission spectroscopy where the sample is melted and volatilized in the arc is this especially true. When this process is further complicated by a violent dissociation and the need for accuracy to correlate trace impurity concentrations with electrical data, the standards problem becomes more difficult. This section will describe the methods used in the preparation of standards for this study and the problems encountered.

2.4.1 Successive Powder Dilution Technique

Spectrographic standards were prepared by the successive powder dilution technique in order to determine the effects of chemical form and particle size distribution of the impurities on spectrographic sensitivity. Separate master mixes of oxides and fine elemental powders were diluted with pure gallium arsenide powder. The standards contained Ag, Al, Cd, Cu, Fe, Ge, Mg, Mn, Ni, Pb, Se, Si, Sn, Te and Zn in the concentration range of 1-100 parts per million. The average particle size of the impurity powders (after sieving through 400 mesh) was 10 microns as determined by optical microscopy and the Coulter Counter. Ten micron particle size powder was found to be the lowest practical limit for ease of handling and reproducibility in the preparation of standards by successive powder dilution. A subsequent statistical analysis of the reliability of standards prepared by this technique showed the need for fine powders in the range of 0.1-1.0 microns as one goes to less than 10 parts per million in impurity concentration. (see Appendix).

Various manufacturers of fine particle size powders were contacted for the procurement of metal and oxide powders in this particle size range. Among these were the Cabot Corporation and the National Research Corporation of Cambridge, Mass. The Cabot Corporation supplied one pound samples of titanium dioxide, aluminum oxide and iron oxide where the basic particulate size was 0.03-0.07 microns. Electronic particle size analysis of these materials as shown in Fig. 6 show an average particle size of 5 microns. This discrepancy was resolved by electron microscopy and x-ray analysis. Basic particulate size was less than 0.1 microns but agglomeration was the cause of the larger particle size. The electron photomicrographs Figs. 7-12 show both the basic particulate size under high magnification and the agglomerate size under low magnification and are representative of these systems. These materials cannot be used in standards stored in glass or plastic vials because of static charge adherence to the container walls.

The National Research Corporation supplies fine metallic powders in the 0.1 micron basic particulate size. These materials are usually stored under organic solvents, inert gaseous atmospheres or with an oxide coating because of their high pyrophoricity. For spectrographic standards, an oxide coating would be required but could not be supplied without fully oxidizing the metals and without control of growth during the stabilization process. The preparation of homogeneous dry mixtures of materials whose particle size spans the region between discrete particle and colloidal particle behavior is beyond the capability of available mixing methods. The problem of homogeneity becomes even more acute when one attempts to prepare a dry mix where one ingredient is present in proportions of 1 part in 10^6 to 10^9 .

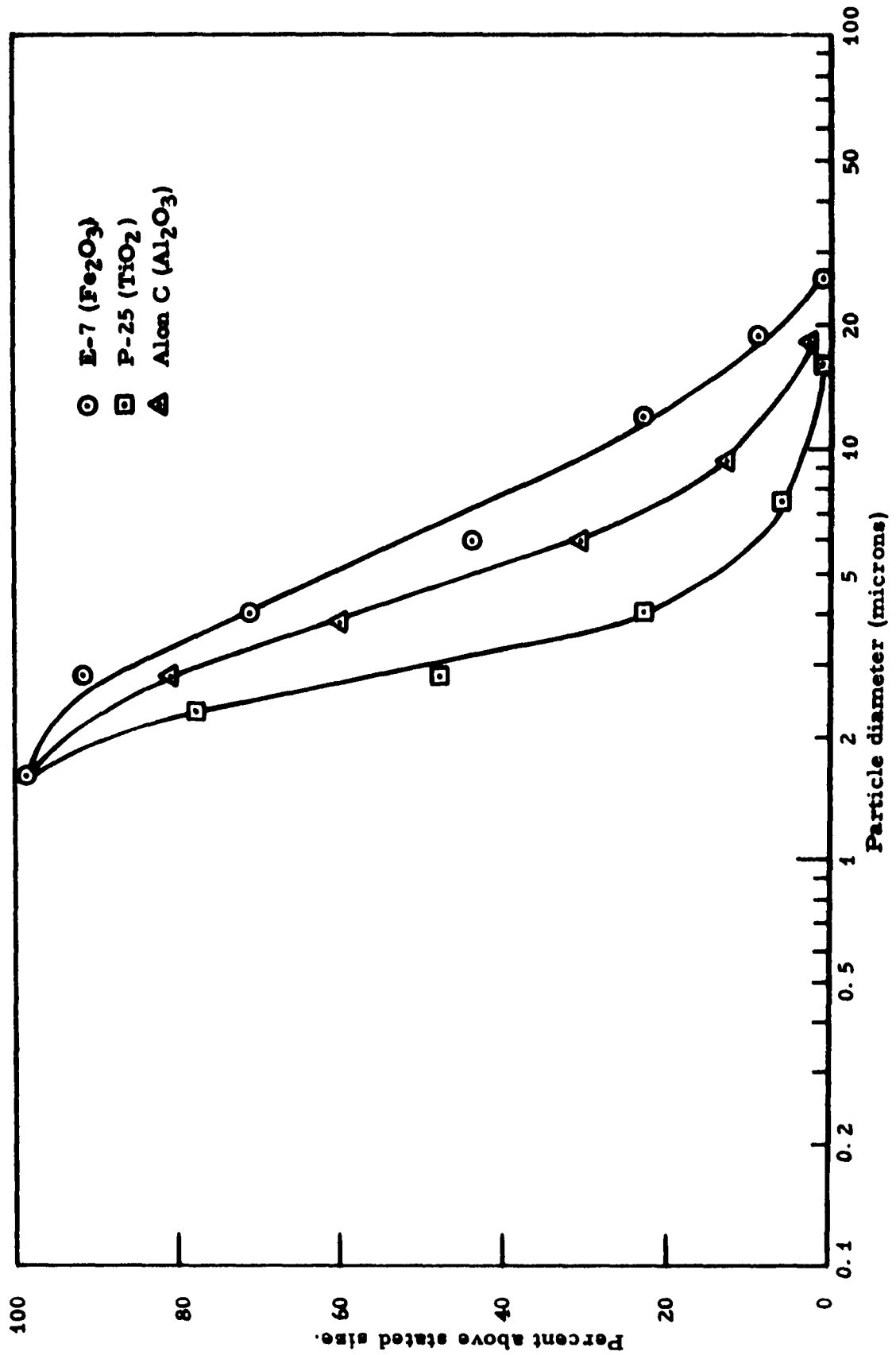


Fig. 6. Coulter counter particle size analysis.



Fig. 7. Electron Micrograph of Cabot Al₂O₃ powder (direct carbon replica preshadowed with platinum metal).

Magnification: 4,900X

Scale: 1 μ

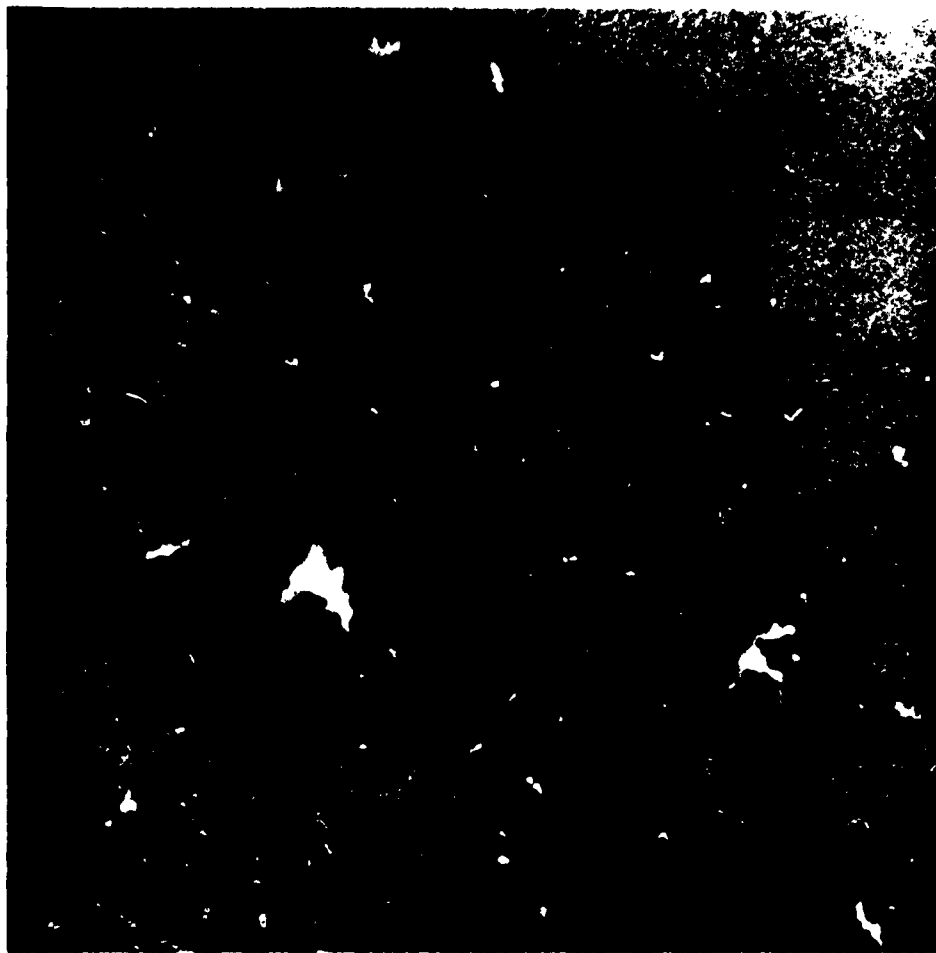



Fig. 8. Electron Micrograph of Cabot Al₂O₃ powder (direct carbon replica preshadowed with platinum metal).

Magnification: 20,200X

Scale: 
μ

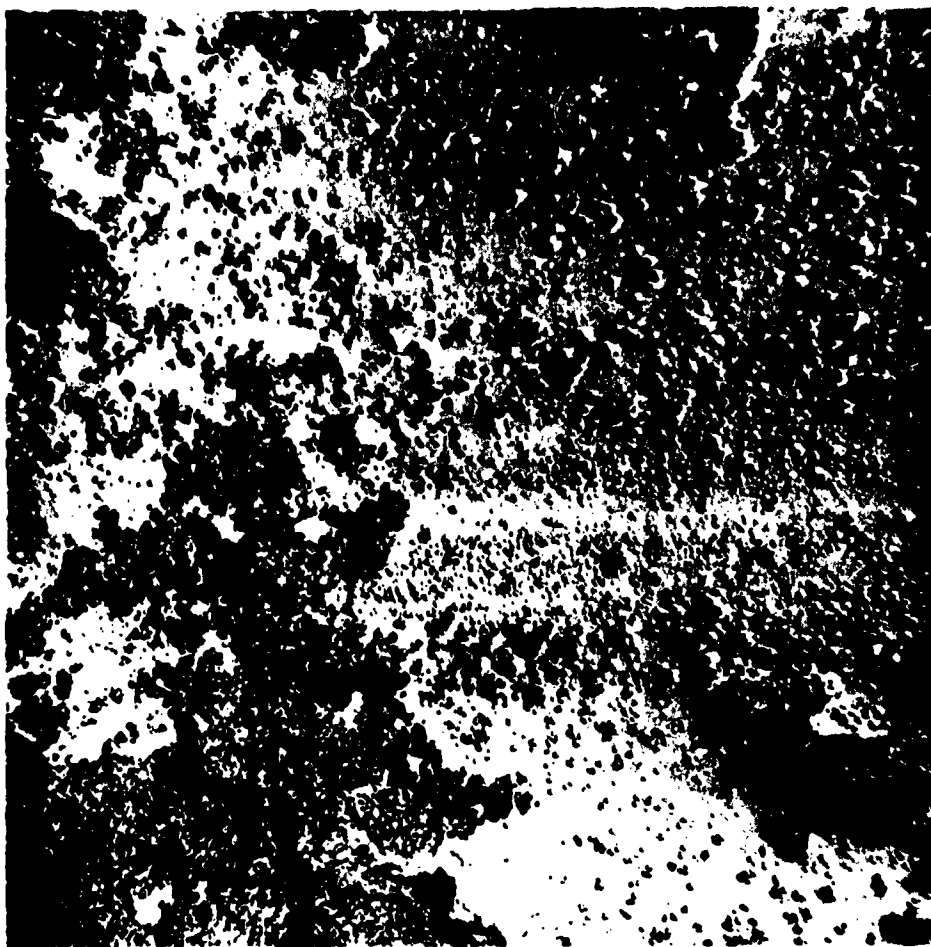


Fig. 9. Electron Micrograph of Cabot Fe₂O₃ powder (direct carbon replica preshadowed with platinum metal).

Magnification: 4,900X

Scale: $\overline{\mu}$

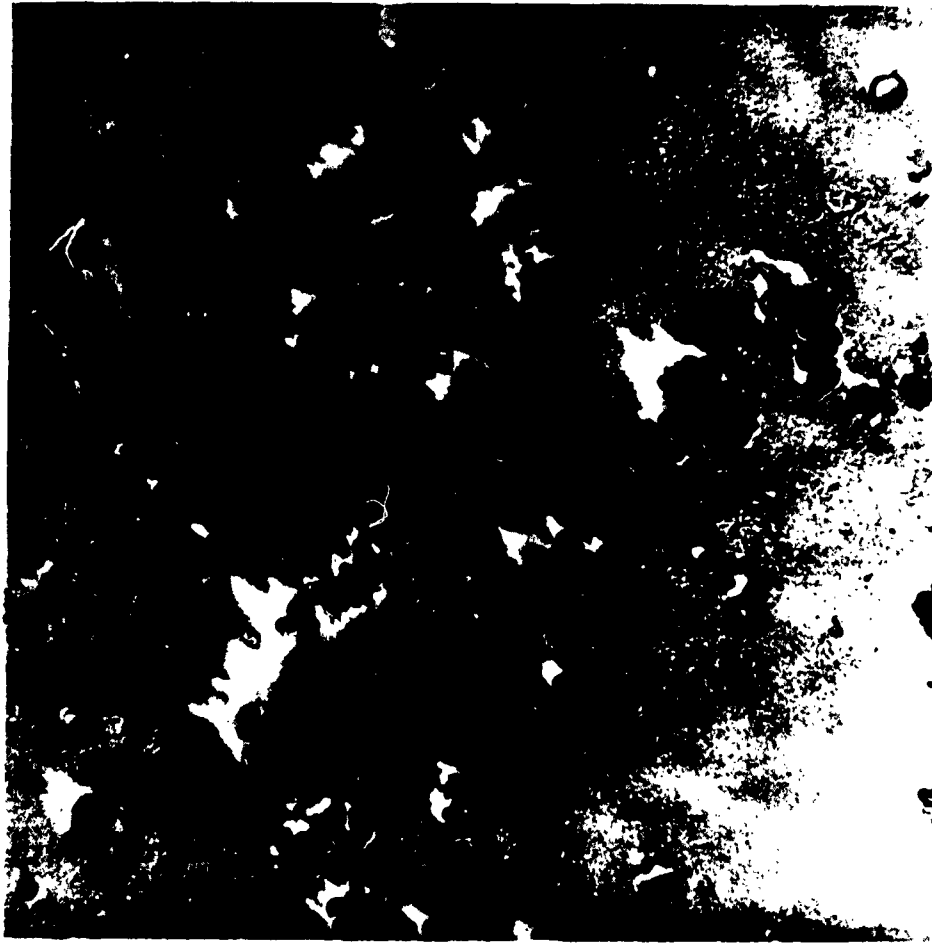
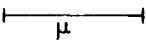


Fig. 10. Electron Micrograph of Cabot Fe₂O₃ powder (direct carbon replica preshadowed with platinum metal)

Magnification: 20,200X

Scale:  μ

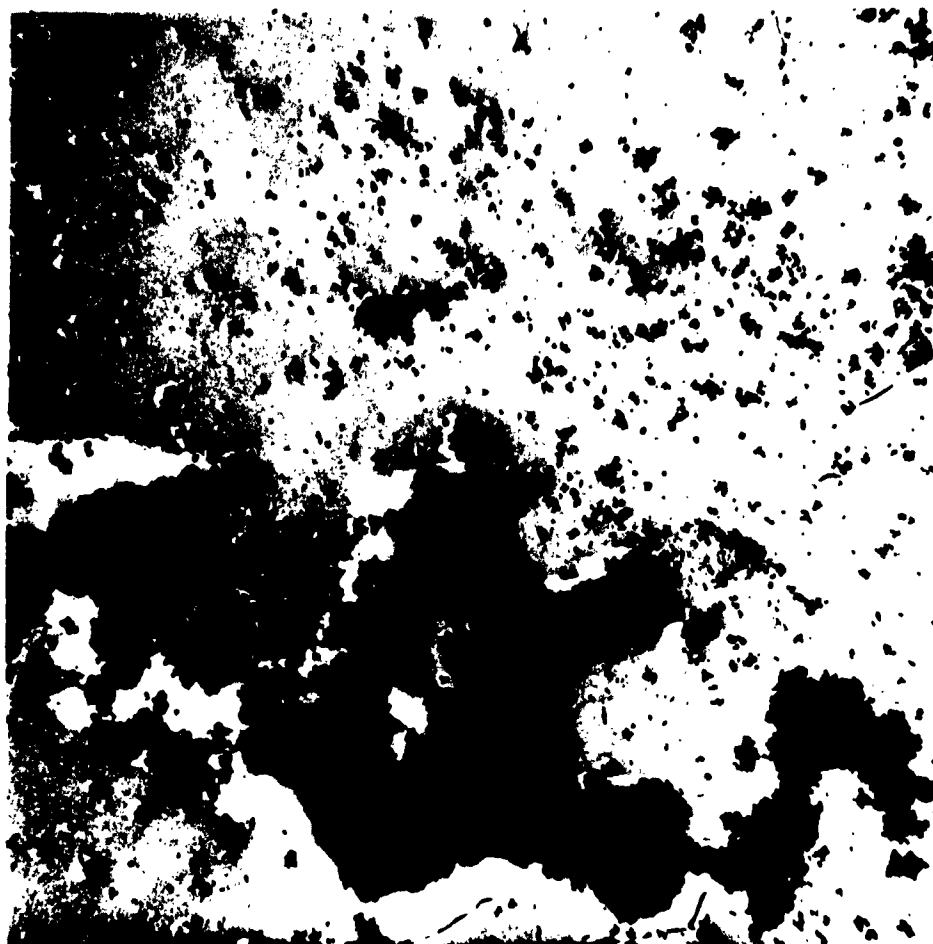


Fig. 11. Electron Micrograph of Cabot TiO_2 powder (direct carbon replica preshadowed with platinum metal).

Magnification: 4,900X

Scale: μm



Fig. 12. Electron Micrograph of Cabot TiO_2 powder (direct carbon replica preshadowed with platinum metal).

Magnification: 20,200X

Scale: μ

2.4.2 Standardization Using the Mass Spectrograph

Six crystals of gallium arsenide whose electrical properties indicate impurity concentration levels from 0.1 to 10 parts per million were selected for mass spectrographic analysis on the spark source Consolidated Electrodynamics mass spectrograph. Four samples were taken from each crystal spanning a ten gram portion in the center. Once standardized, this portion was to be crushed and used in the preparation of spectrographic working curves. One sample has been analyzed thus far. The analysis showed the impurity elements:

	Concentration (ppm)
Si	47
Al	6.3
K	80
N	22
C	500
O	89

Silicon analysis by emission spectroscopy was 40 ppm. Free carrier concentration was $3.0 \times 10^{18} \text{ cm}^{-3}$. Quantitative analysis of the carbon and oxygen present difficulties due to the many different hydrocarbon and hydroxyl charged particles registered on the mass spectrometer plate that must be corrected for instrumental blank. Some difficulties were experienced in determining the optimum excitation conditions so as to minimize consumption of the sample with the attendant condensation on the walls of the sample chamber. Major difficulties were experienced in the monitoring of the beam current and the efficiency of the ion collection. Interference from the rf spark source produced erratic readings of the beam monitor. The collection efficiency of the ions limits the sensitivity of this instrument to 3 ppm for impurities in gallium arsenide.

Therefore it was concluded that the mass spectrograph could not be used for this work until these instrumental difficulties are resolved.

2.4.3 Solid Solution Standards

Solid solution standards, prepared by the diffusion of fine metallic powders into gallium arsenide, were prepared for the impurity elements Cd, Si, Te and Zn in the concentration range of 300, 40, 2000 and 1200 parts per million respectively. Difficulty was experienced with the preparation of a magnesium standard by this method due to chemical interaction with the silica tube. These melts were measured electrically for a 1:1 correlation between electrical data and impurity concentration, crushed and standardized chemically using ultraviolet spectrophotometry, polarography and a spectrographic method employing liquid samples. The analyses checked within 2% of the dopant data. Use was made of this technique for the preparation of a standard of silicon in gallium arsenide. However, correlation with electrical data was prevented by the complex interactions of silicon, carbon and oxygen in the matrix material. The sample could not be analyzed for silicon content by reliable wet chemical techniques necessitating standardization by spark source mass spectrometry and an alternate emission spectrographic technique. The concentration of silicon as averaged between these two independent methods was 43 ± 4 parts per million. This material was not considered a reliable standard because of the uncertainty of silicon content. These standards were used to prepare working curves shown in Figs. 13 and 14.

2.4.4 Contamination and Blanking Problems

Due to the fact that standards for the spectrographic method of analysis of trace impurities in gallium arsenide have to be made with the impurities in solid solution, the blanking problem for impurities introduced

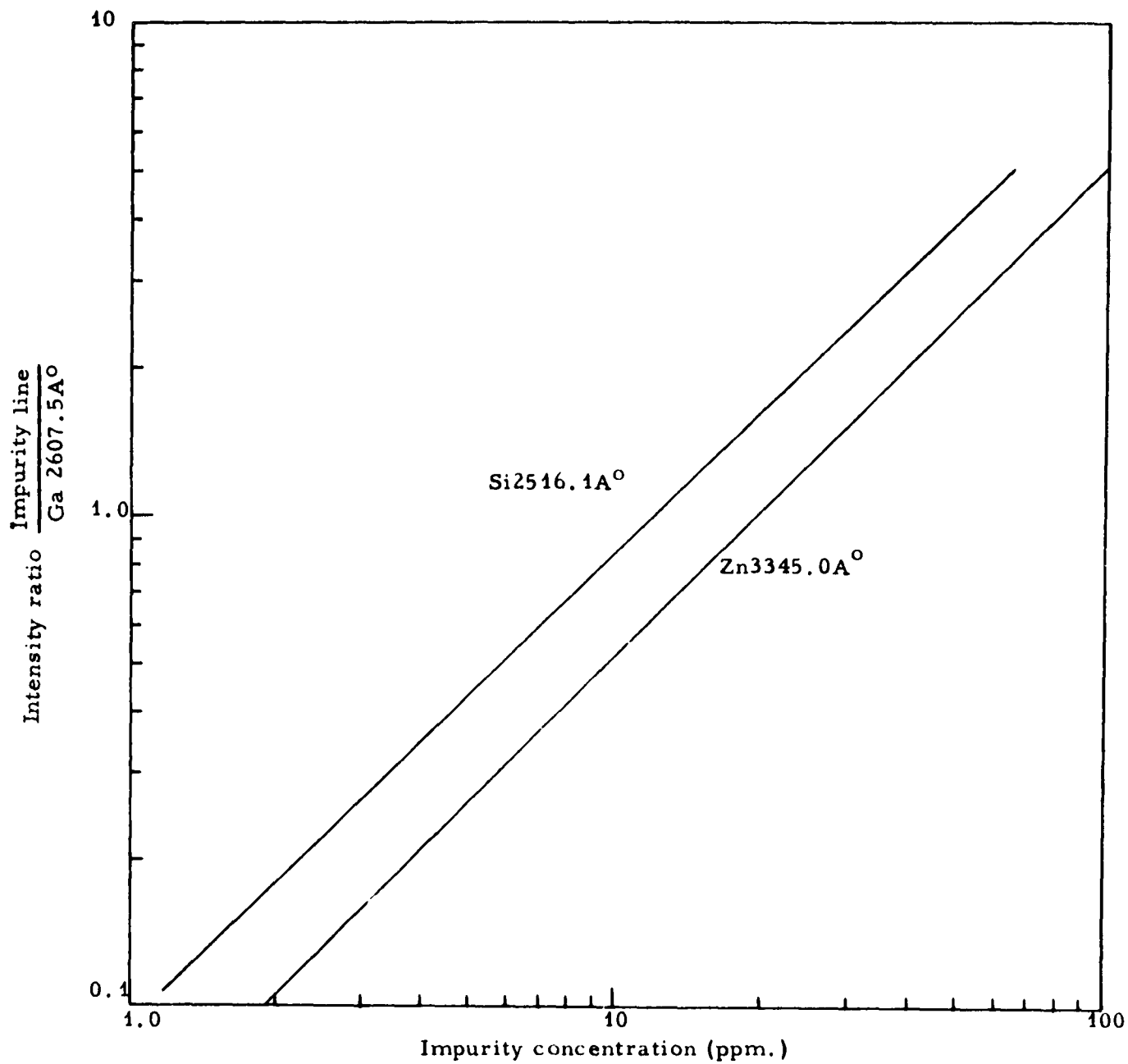


Fig. 13. Spectrographic working curves -- solid sol'n stds. in GaAs

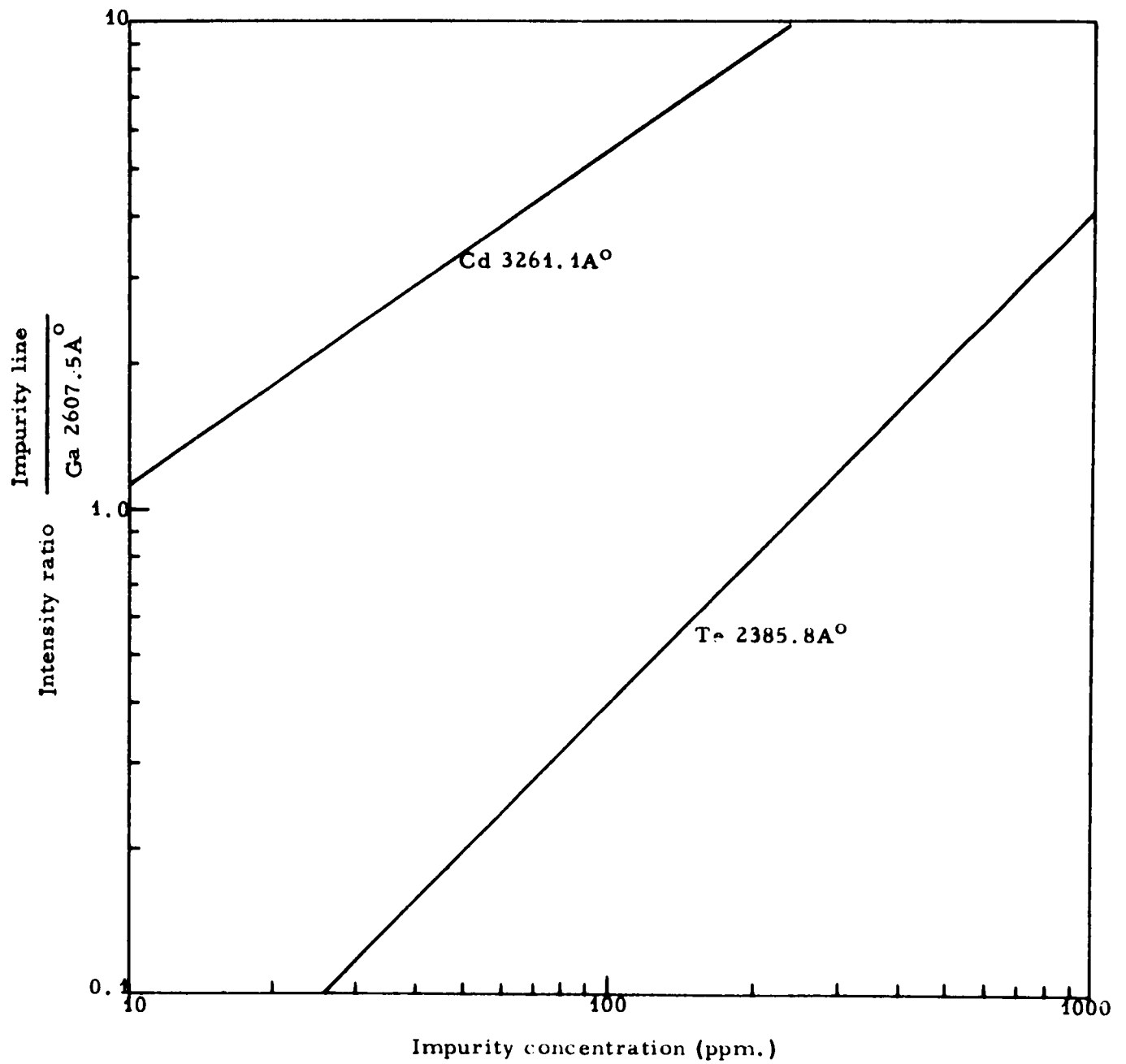


Fig. 14. Spectrographic working curves -- solid sol'n stds. in GaAs

during the grinding and arcing operations becomes exceedingly difficult. The volatilization characteristics of impurities added during these operations are not representative of the volatilization behavior of impurities from solid solution during the arcing because of the differences in chemical form and solubility. Therefore, the effect of impurity blank is indeterminate. The only possible control is to keep the impurity pickup to a minimum by constant monitoring with moving plate studies.

Powdering gallium arsenide in plastic vials with steel balls and in tungsten carbide vials and balls contributed Al, Cu, Fe, Mg, Na, Pb, Si and Zn as heavy contaminants. Tungsten carbide was the principal source of impurity pickup. Pickup from grinding in a boron carbide mortar and pestle (trade name "Norbide") produced a trace of boron as the contaminant.

United Carbon preform C-425 with a 1966 counter electrode and the National Carbon SP1001 with an SP1004 counter electrode were used in these studies, with their burning characteristics being similar. The National Carbon product was purer than the other, the impurities in both being Al, Ca, Cd, Cu, Fe, Mg and Si. Care should be taken not to place any emphasis on impurity concentration levels in the electrodes which are expressed in parts per million. This is totally erroneous being dependent upon representative standards and varying widely because of the effects of chemical reactivity of molten matrices with the electrodes.

2.5 PREPARATION OF SPECTROGRAPHIC WORKING CURVES OF IMPURITIES IN GALLIUM ARSENIDE

Spectrographic working curves were prepared using the solid solution standards for Cd, Si, Te and Zn. The excitation conditions set forth in Table I, and the working curves are shown in Figs. 13 and 14.

The limits of detection for these impurities could not be lowered further by changing the spectrographic parameters. It is felt that these limits are governed by the volatility conditions the matrix imposes upon solid solution standards. The curves are reliable to $\pm 10\%$. Analyses were performed on zinc-doped gallium arsenide samples supplied by Battelle Memorial Institute with very good correlation with the electrical and dopant data.

A discussion of the working curves of the oxide and metal powder standards is in order because of the interesting results that came to light during the course of the study. Studies on the reproducibility of working curves as a function of the loading procedures demonstrated the need for control of the sample weight and packing in the electrode cup. Oxide powder standards loaded with a stainless steel micro spatula, electrically grounded, provide working curves that are more reproducible ($\pm 10\%$) than those loaded with an ungrounded spatula ($\pm 25\%$). Elemental powder standards containing iron and nickel powders in varying concentrations must be loaded with a platinum spatula to provide good reproducibility ($\pm 10\%$) in the working curves. The stainless steel spatula removed iron and nickel powders presumably by magnetic attraction. These observations taken in the 1-100 parts per million concentration range show the need for rigorous handling procedures. Since oxide powder standards were not representative of the volatilization behavior of impurities in solid solution in the gallium arsenide, their use was discontinued. However, the observations should prove of value in other studies.

2.6 THE SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF TRACE IMPURITIES IN GALLIUM ARSENIDE

The spectrographic parameters used in the trace spectrographic method for the determination of trace impurities is shown in Table I. This

is the result of extensive researches on the many aspects of the problem, each of which has been detailed in this report. Since an analytical method is of no value unless there is a correlation with electrical behavior in the case of semiconductors, we have worked in close liaison with Battelle Memorial Institute and the research group doing gallium arsenide work at this laboratory. A few samples of gallium arsenide containing zinc have been analyzed and the results are as follows:

<u>Sample No.</u>	<u>Zinc Concentration (ppm)</u>	
	<u>Elec. Meas.</u>	<u>Emiss. Spect.</u>
107 F. F.	170	152
Battelle 359-3	20	21
Ht. Treat Rms #1	4.5	4.7

There is very good agreement on the zinc analysis. However, there is poor agreement in the analysis for silicon in the gallium arsenide. In every case, the silicon concentration by spectrographic analysis has shown a larger impurity concentration than the electrical data. It has been shown by Battelle Memorial Institute that gallium arsenide containing 10^{18} carriers/cm³ from silicon can approach intrinsic behavior if heated in an oxygen atmosphere. Currently, investigations are being conducted to determine the possible interactions between carbon, oxygen and silicon.

Work on other impurities in gallium arsenide requires additional solid solution standards. The preparation, characterization and standardization by an alternate chemical method could not be performed within the effort covered by this contract. Battelle Memorial Institute has agreed to supply many solid solution samples containing impurities of interest and the work is being continued and extended under company support.

3. CONCLUSIONS AND FUTURE WORK

The research that was done on the many facets of this problem has brought to light a number of interesting results. They are summarized as follows:

1. Spectrographic standards prepared by successive powder dilution of a mixture of oxides or elemental powders are not representative of solid solution standards in the case of gallium arsenide. This factor should be investigated for every matrix. The powder dilution technique cannot be used below the 1 part per million level except in special cases. In the silicon carbide study, the limits of spectrographic sensitivity were lowered due to long and tedious working of the standards in a boron carbide mortar and selective volatilization. Since very small particle size powders ($< 1\mu$) are unavailable and difficult to handle, the preparation of accurate standards by powder dilution in the 1 part per million range is questionable. Solid solution standards or liquid techniques present the only reliable approach to adequate standards for ultratrace emission spectroscopy.
2. Electronic particle size analysis by the Coulter Counter is a rapid means of obtaining particle size distribution but suffers from a practical lower limit of 1μ and agglomeration effects often encountered in sedimentation procedures. Since the total number of particles per sample is obtained by extrapolation, the presence of a skewed population in the small particle size range ($< 1\mu$) results in an inaccurate estimate of the effect of the smaller sized particles. However, these limitations

will only become evident in small particle size work.

3. The mass spectrograph has the capability of comprehensive analysis for 40-50 elements including the gases and halides. At the present time, it suffers from poor sensitivity (3 ppm) for impurities in gallium arsenide, unreproducible beam monitoring and low sample capacity. These problems are currently under investigation.
4. Emission spectroscopy can be an ultratrace tool. The emission spectrograph possesses adequate sensitivity for analyses in the parts per billion range. A principal obstacle is in the preparation of standards. A suggested approach is as follows:

A number of different samples (4-6) of a matrix should be run on the spark source mass spectrograph, which can give absolute composition. In any two of these samples, wet chemical analyses should be done on two different impurities (1 in each sample). These impurity concentrations can be used as references to determine the concentrations of the other impurities and as checks upon each other.

The analyzed samples can then be used as standards in emission spectroscopy for the determination of spectrographic parameters and working curves. Once this is accomplished the emission spectrograph can assume the major work load.

5. Trace emission spectrographic research should continue on solution of the problems of the very volatile impurities and the refractory matrices. The solution of the problem of the volatile impurities should be attempted using either a solid state dc arc source in inert atmospheres or pulsed laser

source (ruby) where control of the source is accomplished by defocusing. The solid state source would provide instantaneous power. The refractory matrix problem requires high temperature sources such as plasma or laser sources.

4. PERSONNEL

The gallium arsenide study was under the direction of D. J. Bracco. The engineering staff on the project included D. J. Bracco, R. L. Rupp, P. H. Keck and G. H. Morrison. Technicians on the project were E. Kulesz and R. E. Everett.

Analytical and preparative services were as follows:

Wet Chemical Analyses	-	R. Weberling
Emission Spectroscopy	-	S. Weisberger
Computer Services Department	-	S. Barton
Mass Spectrometry	-	R. Wallace, J. Roboz
X-ray Diffraction and Optical Microscopy	-	C. Tufts
Preparation of Gallium Arsenide Crystals and Electrical Measurements	-	J. Black

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6. PAPERS PUBLISHED

1. Morrison, G.H. , "Proceedings of the Conference on the Ultrapurification of Semiconductor Materials," Pergamon Press, New York, 1961.

7. TALKS PRESENTED

1. "Determination of Ultratrace Impurities in Semiconductor Materials" by G.H. Morrison, Conference on the Ultrapurification of Semiconductor Materials, April 11-13, 1961, Boston, Mass.
2. "The Use of Controlled Atmospheres in Emission Spectrography" by R. L. Rupp, General Motors Spectrographic Conference, April 24, 1961, Detroit, Michigan.
3. "Ultratrace Emission Spectroscopy" by G.H. Morrison and R. L. Rupp, Annual Meeting A.S. T. M. , June 28, 1961, Atlantic City, N. J.

APPENDIX

Statistical Analysis of the Effect of Impurity Particle Size on the Reliability of a Standard Prepared by Powder Dilution

- S. Barton -

Random samples are drawn from a large batch of material consisting of a uniform mixture of two substances A and B. The concentration of A in B is assumed to be known precisely and lies between 10^{-6} and 10^{-9} grams of A per gram of B. The sample size is small relative to the batch size and the sample contains a large number of particles. However, since substance A is present in such a small amount, relatively few particles of A may occur in the sample. Since there are difficulties in obtaining and handling powders whose particle size range lies in the region between colloidal and discrete particle size behavior, it would be preferable to use as coarse a powder as possible provided that there is a high probability that the concentration of A in any sample would lie within narrow limits of the batch concentration. This latter constraint is important because the samples are to be used as standards to determine the concentration of A in B. The determination is known to be imprecise for such low concentrations. In order that there be a high probability that deviation from the expected number of particles of A in a sample be small, the average number of particles of A in a sample must be so large that deviations due to the distribution of particle sizes be negligible.

The number of ways in which r particles of substance A can occur in a sample of n particles is equal to $\frac{n!}{r!(n-r)!}$. If p is the fraction of substance A, and $q = 1-p$ the fraction of substance B present in the batch, then the probability, P_r , of any sample containing exactly r particles

of A is given by

$$P_r = \frac{n!}{r! (n-r)!} q^{n-r} p^r,$$

the equation of the Bernoulli Distribution.

Let $m = pn$ be the expected (average) number of particles in a sample. If n is large and $m \ll n$, then $(1 - \frac{m}{n})^{-r} \approx 1$

$$q^{n-r} = (1 - \frac{m}{n})^n (1 - \frac{m}{n})^{-r} \approx (1 - \frac{m}{n})^n$$

Replacing $n!$ and $(n-r)!$ with Stirling's approximation

$$(X!) = (\frac{X}{e})^X \sqrt{2\pi X} \text{ gives}$$

$$P_r = \frac{n^r}{r!} (1 - p)^n p^r = \frac{m^r}{r!} (1 - \frac{m}{n})^n = \frac{m^r e^{-m}}{r!}$$

which is the equation of the Poisson Distribution.

Figures 1 and 2 are plots of the probability, $P_m^{\dagger d}$, that the percent deviation, $\frac{d}{m} \times 100$ will not be exceeded in any sample for which the expected number of particles is m . Figure 3 is a plot of the percent deviation that will not be exceeded in 99 out of 100 samples vs the expected number. For convenience, the curves are plotted as if the distribution were continuous, although it is in fact discrete. A program to calculate the values for these curves was written for the Bendix G-15D computer since tabulated values were not available for such large values of m .

In the present case, maximum sample size is 0.045 grams, the minimum mean diameter of substance A is 0.1 microns, and the density of substance A is approximately 6 grams/cm³.

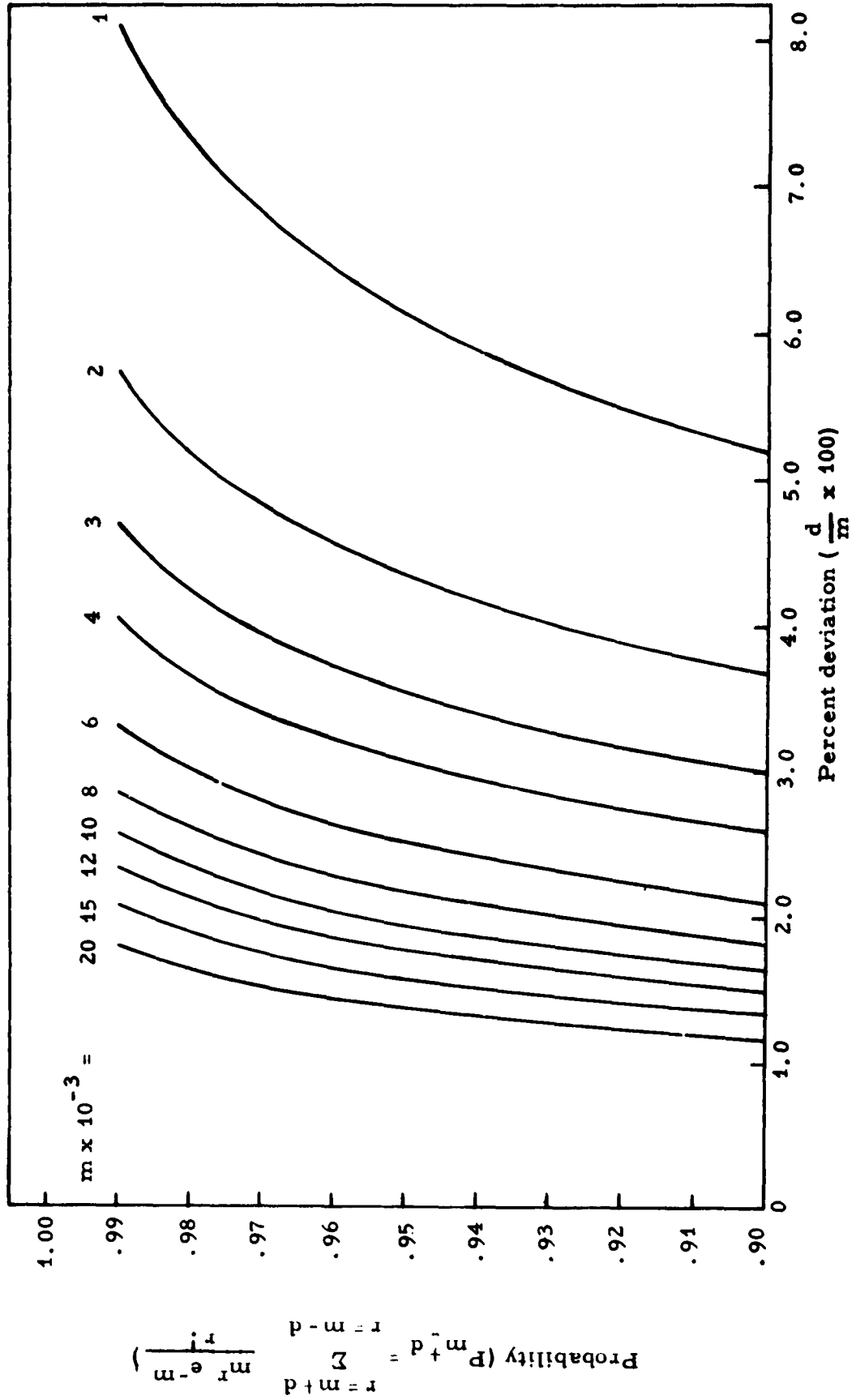


Fig. 1. Cumulative poisson distribution

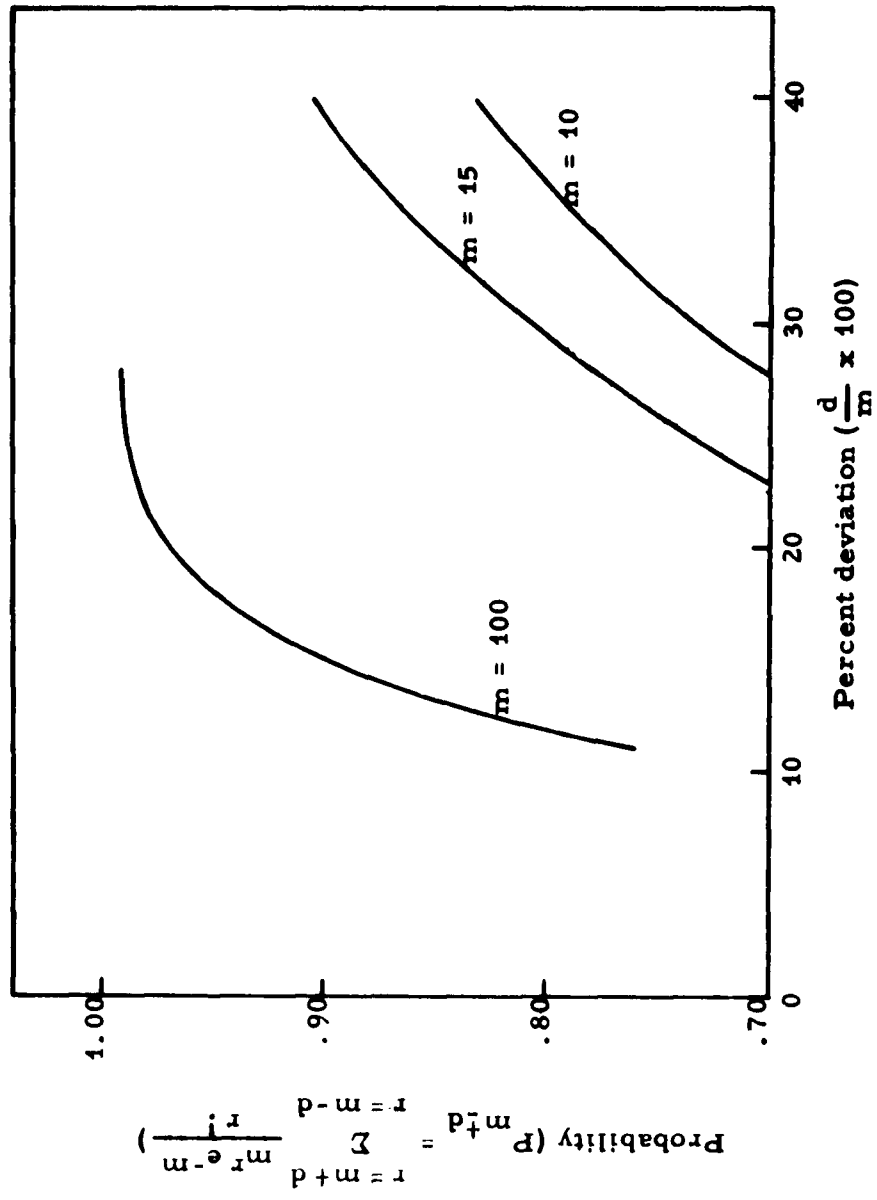


Fig. 2. Cumulative poisson distribution.

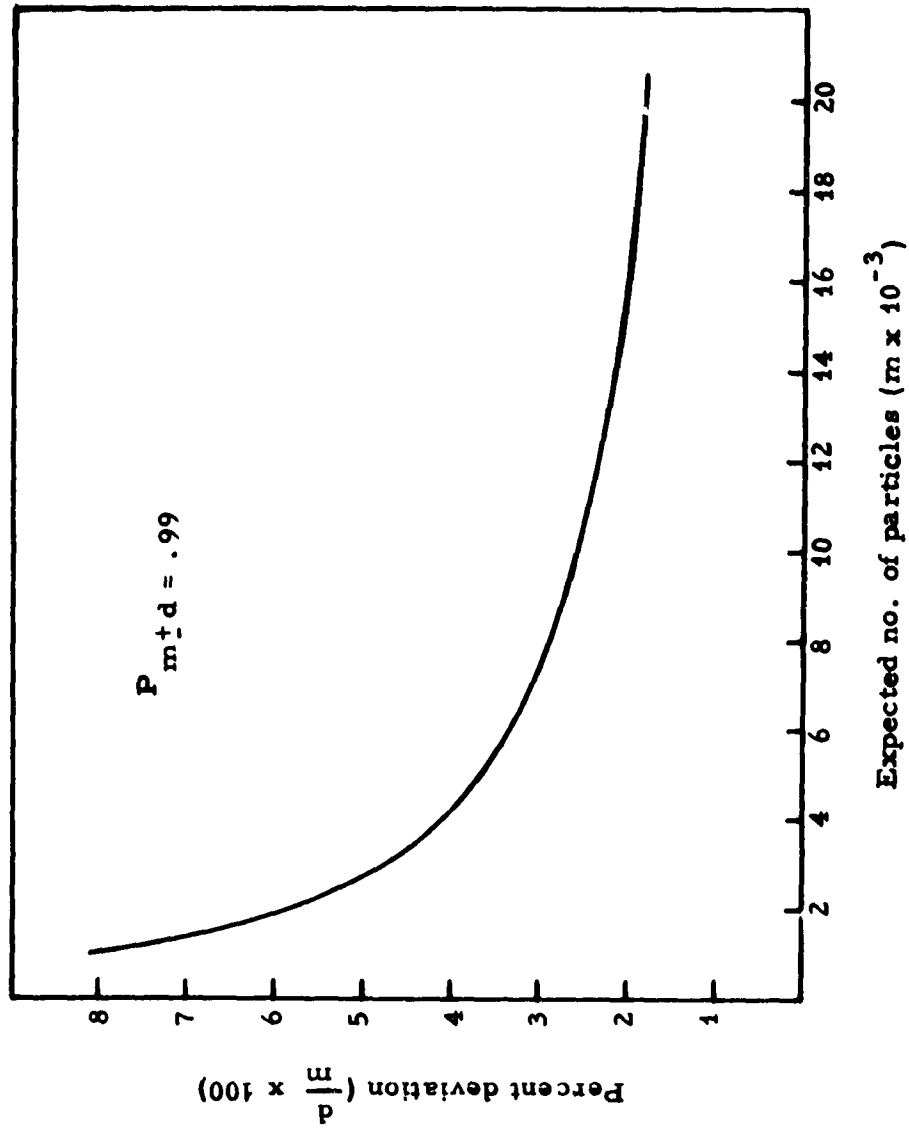


Fig. 3. Percent deviation as a function of the expected no. of particles.

At the lowest concentration of 10^{-9} g A/g.B, the amount of A expected in a sample is 4.5×10^{-11} g. The mass of the average 0.1 micron particle is $6 \frac{\pi}{6} (10^{-5})^3 = 3 \times 10^{-15}$ g. The expected number of particles of A is $\frac{4.5 \times 10^{-11}}{3 \times 10^{-15}} = 1.5 \times 10^4$ particles.

For 1 micron particles, the expected number would be $\frac{4.5 \times 10^{-11}}{3 (10^{-4})^3} = 15$ particles.

Examining more closely the condition $m \ll n$ which reduces the Bernoulli Distribution to the Poisson shows that n must be of the order of m^3 or greater. At the lowest concentration and for $m = 15000$, this would require the mean diameter of substance B to be unreasonably small (~ 0.05 microns). However, it can be shown that if m is sufficiently large to be approximated by Stirling's formula, then

$$\left[\frac{P_{(r=m, n=m^2)}}{P_{(r=m, n=m^3)}} \right]^2 = 1 - \frac{1}{m} + \frac{1}{m^2} - \dots$$

Therefore, for m sufficiently large, the Poisson formula is a good approximation to the Bernoulli for $n = m^2$, which at the lowest concentration results in a reasonable diameter for substance B (~ 6 microns). The above result also indicates that the larger the value of n relative to m , the more peaked the distribution of P_r around m . That is, the smaller n (larger mean diameter of substance B), the larger the probability that a given deviation will be exceeded.

Deviations due to the distributions of particle size may be estimated as follows:

$$\tilde{\mu} = \bar{\mu} \pm \frac{2.58}{\sqrt{m}} \text{ with probability } 0.99, \text{ where } \tilde{\mu} \text{ is the observed}$$

average mass of A particles in a sample containing m such particles whose masses are normally distributed with mean $\bar{\mu}$ and standard deviation σ .

The percent deviation which will not be exceeded in 99 of 100 samples is

$$\pm \frac{2.58}{\sqrt{m}} \times 100 \text{ assuming } \sigma \approx \bar{\mu} \text{ and } m = 15000,$$

$$\% \text{ dev.} = \pm \frac{2.58 \times 100}{\sqrt{15000}} = \pm 2.1\%$$

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